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ABSTRACT

To aid in the calculation of probable temperature rises in the steam jetting of Purex organic streams, approximate specific heats have been determined for some pure solvents, diluents, and uranium-solvent-diluent solutions. The following values were obtained:

	Liquid	Specific Heat - Cal/g/°C 25°C	61°C
(1)	100% Amsco 123-15	0.48	-
(2)	100% TBP	0.41	-
(3)	30% TBP in Amsco	0.48	0.39
(4)	30% TBP in Amsco, 0.2 M in U	0.43	-
(5)	30% TBP in Amsco, 0.5 M in U	0.41	0.37
(6)	Socony Vacuum - 478	0.46	-
(7)	Gulf-BT	0.45	-

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INTRODUCTION

Approximate specific heats at 25°C and 61°C have been determined for some Purex organic solvents and diluents to aid in calculations of probable temperature rises during the steam jetting of organic streams.

METHOD

The technique for the accurate determination of specific heats is exacting and difficult. In the present work, an error of ± 10 - 15% was considered acceptable in order to obtain values rapidly. Accordingly, a relative method was chosen in which a constant quantity of heat was supplied to equal volumes of a standard of known specific heat, and to the unknown in an insulated system of fixed geometry.

Calculations may be made from the following:

A. The temperature changes in unit time

$$(\text{sp ht})_2 = \frac{(\text{sp ht})_1 \, (\Delta T)_1 \, (V_1) \, (d_1)}{(V_2) \, (d_2) \, (\Delta T)_2} \tag{1}$$

or

B. The time intervals required for effecting the same temperature increase:

$$(\text{sp ht})_2 = \frac{(\text{sp ht})_1 \, (V_1) \, (d_1)}{(\Delta t)_1} \times \frac{(\Delta t_2)}{(V_2) \, (d_2)} \tag{2}$$

where sp ht = specific heat in cal/g/°C.

ΔT = temperature rise in unit time

V = volume in cc

d = density in g/cc

Δt = time interval for unit temperature rise

subscripts (1) refer to the standard

subscripts (2) refer to the unknown

These equations represent approximations of the specific heats; there is no attempt, for example, to include a term for the heat capacity of the calorimeter.

In these experiments water was chosen as the relative standard; densities were determined on a Fisher-Davidson gravitometer.

COMPARISON STANDARDS

It had been desired to evaluate the accuracy of the method by determining the specific heats of several known liquid organic compounds. Because, however, of the difficulty in obtaining pure compounds whose physical properties at least approximated the Purex solvents, and whose specific heats are available in the literature, only two standards, benzene and isooctane, were used. The results are recorded in Table I. The per cent differences were used as empirical corrections to the specific heats determined for the Purex liquids.

Table I. Specific Heats of Comparison Standards

Compound	Specific Heat - cal/g/°C 25° Literature Value	25° Found[3]	25° % Difference	61° Literature Value	61° Found[3]	61° % Difference
Benzene	0.411[1]	0.48	+14	0.445[1]	0.47	+6
Isooctane	0.494[2]	0.57	+14	-	-	-

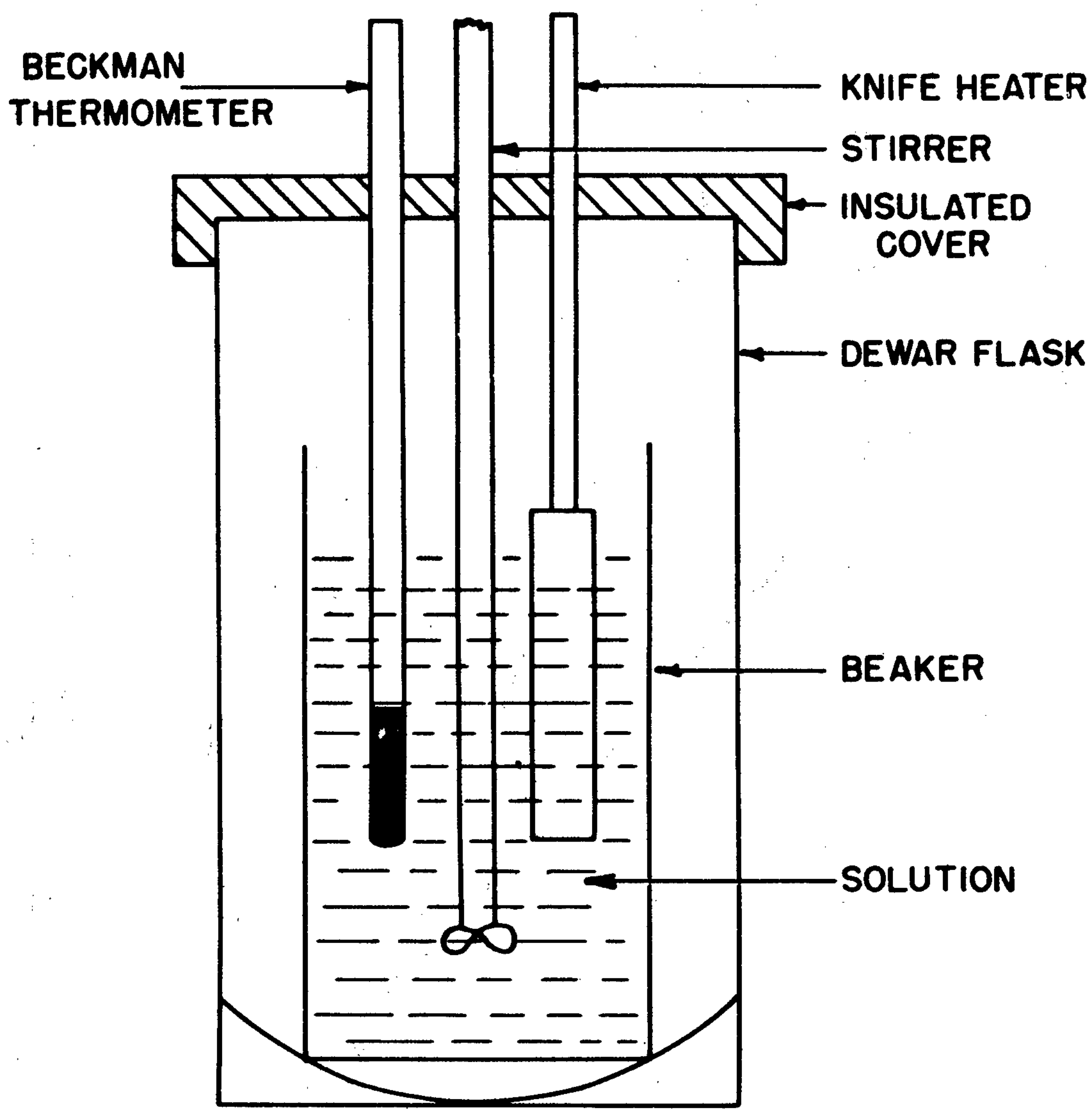
(1) Interpolated from values at various temperatures in the Chemical Rubber Handbook.

(2) Only a value at 20°C reported by Osborn and Ginnings, J. Res. Nat. Bur. Stds., 39, 453-77 (1947).

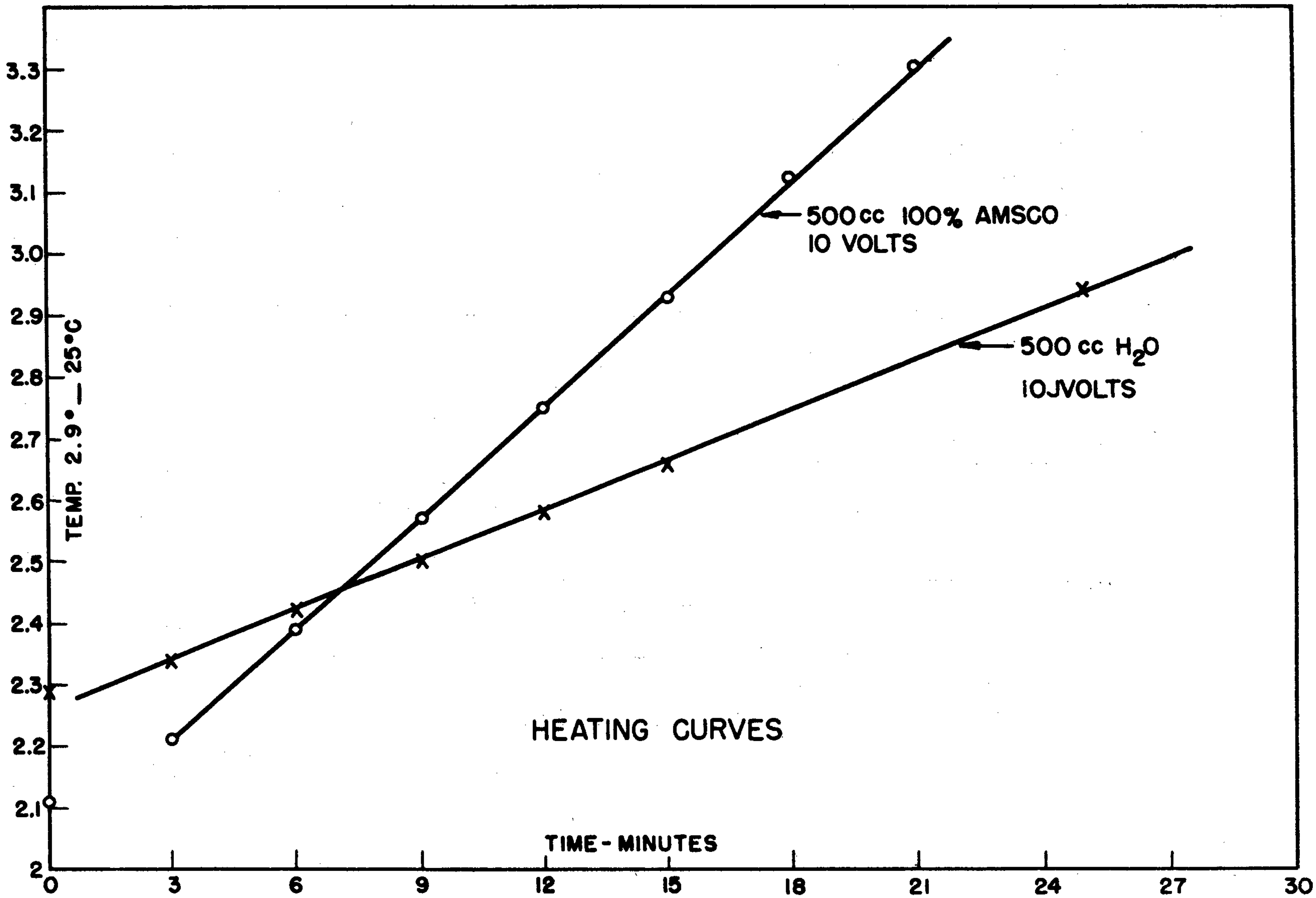
(3) Each value is the average of duplicate runs which differed by 1 - 2%.

APPARATUS

Figure K-6A3842 shows the experimental apparatus. A 4.5 x 8-inch Dewar flask was used to hold a 600 ml beaker containing the liquid. The knife heater was rated at 125 watts. The heat supplied to the liquid was limited and was maintained constant by regulating the operating voltage with a Variac. Some runs on the pure liquids were made without a glass shield over the heater. But because the uranium solutions attacked the metal blade of the knife heater, a shield was found necessary. A Beckman differential thermometer set for the desired temperature range was used to follow the rate of heating.



APPARATUS FOR DETERMINING SPECIFIC HEATS


500cc 100% AMSCO
10 VOLTS
500 cc H_2O
10JVOLTS
HEATING CURVES
TEMP. 2.9° _ 25°C
TIME - MINUTES
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
0
3
6
9
12
15
18
21
24
27
30

PROCEDURE

General

Trial runs with water established a convenient combination of liquid volume, operating voltage, and depth of immersion of the heater blade. Five replicate runs were made for the water calibration (see Table II) and duplicate runs were made for each organic liquid.

Specific Heats at 25°

Runs were made with 500 cc of liquid measured in a graduate. About two inches of the heater blade were immersed, and it was operated at ten volts. Prior to heating, temperature readings were taken every five minutes until a constant value was obtained. About twenty minutes were required for this equilibrium temperature to be established. After heating was started, temperature readings were taken every three minutes. With the exception of the first readings, there was a linear temperature response over a period of thirty minutes. Equation (1) was used to calculate the specific heats with "unit time" taken as fifteen minutes.

Table II. Calibration Values with 500 cc of Water

Sp ht H_2O at 25°C	= 0.9983 cal/°C/g
Density H_2O at 25°C	= 0.9971 g/cc
Wt H_2O	= 498.55 g
Ht Capacity	= 497.70 cal/°C

	(Δ Temp) 15 min		(Δ Temp) (ht capacity)
(1)	0.40		199.08
(2)	0.37		184.15
(3)	0.44		218.99
(4)	0.40		199.08
(5)	0.42		209.03
		Avg. =	202.06
		S =	6.4 pts/100

For the uranium solutions the glass shield was used over the heater which was operated at 17 volts with 450 cc of solution. The system was recalibrated with water for the new volume, geometry, and heating rate. Check runs showed that results with and without the glass shield had the same agreement as duplicates (see note 6, Table III). Corrected specific heat values at 25° are listed in Table III.

Specific Heats at 61°C

The glass shield was used in all determinations. Trial runs established that the heater, operated at 45 volts with 450 cc of liquid, would provide a rate of heating which was fairly rapid but linear over a 1.5 degree temperature rise. Slower heating rates at lower voltages were nonlinear. The volume of liquid was measured at 25°C in a graduate, and the density was determined at this temperature. If it is assumed that the temperature coefficients of expansion of the various solutions are not greatly different, the heater surface in each of the liquids will be essentially the same at 61°C. It was felt, further, that any error introduced by not measuring the volumes and densities at 61°C would not exceed the error due to the method.

The liquid was poured into the beaker and heated to about 60°C on a hot plate. The beaker was then placed in the Dewar flask and covered. To establish thermal equilibrium, heating was started and was continued until the system attained a temperature of about 62°C. The heater was then turned off, and the temperature was allowed to fall to about 60°C. Heating was started again; from 60.5° to 62.5°C, temperature readings were taken, every minute for water, and every thirty seconds for the organic liquids. Equation (2) was used to calculate the specific heats with "unit temperature" taken as 1°. Corrected specific heats are listed in Table III.

Table III. Corrected Specific Heats of Organic Solvents and Diluents

	Solution	Uranium Molarity	Specific Heat[2] cal/gm/°C 25°C	61°C
(1)	100% Amsco 123-15	0	0.48	-
(2)	100% TBP	0	0.41	-
(3)	30% TBP in Amsco	0	0.48	0.39
(4)	30% TBP in Amsco	0.2[1]	0.43	-
(5)	30% TBP in Amsco	0.5[1]	0.41	0.37
(6)	Socony Vacuum - 478	0	0.46	-
(7)	Gulf BT	0	0.45	-

(1) A 100% saturated solution of uranium in 30% TBP is about 0.51 M in uranium. This solution was prepared by dissolving 160 g of UNH in 600 ml of 30% TBP and centrifuging to remove the water. The 0.2 M U solution was made by dilution of the saturated solution with 30% TBP in Amsco. Uranium concentrations were determined spectrophotometrically.

(2) Each value is the average of duplicate runs which differed by 1 - 3%, except 2 and 5 at 25° for which the difference was 11%.

DISCUSSION

In the experiments with the comparison standards, an attempt to use cyclohexanol gave rise to an anomolous value for the specific heat. The viscosity of cyclohexanol is considerably higher than the other comparison standards used and the Purex liquids. It appears that viscosity influences the experimental specific heat values, possibly by affecting the heat transfer properties. Thus the empirical corrections made on the basis of the values for the comparison standards apply only where there is not a large difference between the viscosities of the comparison standards and the "unknown" liquids. This situation is achieved with all of the Purex liquids with the possible exception of 100% TBP. The viscosity effect would be less at 61° than at 25°.

Solutions of uranium in 30% TBP-Amsco apparently show a decrease of specific heat with increasing uranium concentration, and with increasing temperature.

CONCLUSIONS

The experimental values of specific heats are considered adequate for preliminary calculations of probable temperature rises in the steam jetting of Purex organic streams. On the basis of specific heats, no choice can be made between the three diluents, Amsco 123-15, Socony Vacuum - 478, or Gulf BT.